trans-2,2′-Bi(1-phenyladamantylidene): The Most Twisted Biadamantylidene

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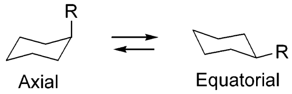
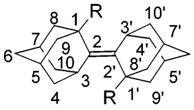
The Grignard coupling of 2,2-dibromo-1-phenyladamantane gave *trans*-2,2′-bi(1-phenyladamantylidene) (**1-Ph**). Single-crystal X-ray analysis indicated that **1-Ph** has a 23.2° twisted double bond, which is much more distorted than that of parent 2,2′-biadamantylidene (**1-H**) and that of the ethyl-substituted derivative (**1-Et**). A cyclic voltammogram showed a reversible electron oxidation wave at 0.87 V vs Fc/Fc$^+$, which is 0.19 V lower than **1-H**, indicating a significant increase in the HOMO energy level due to the distortion. The reaction of **1-Ph** with 0.9 equiv of bromine gave an intramolecular Friedel−Crafts alkylation product, while bromination of **1-H** and **1-Me** has been reported to give a bridged bromonium ion and a rearranged product, 2-(1-methyl-2-adamantylidene)-4-bromotricyclo[5,3,1,0$^{3.9}$]undec-4-ene, respectively.

Introduction

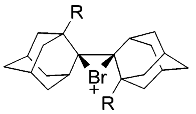
2,2′-Biadamantylidene (**1-H**) is the first olefin to be isolated as a stable bridged bromonium salt **2-H**, which is known as the intermediate of bromination.[1] The success is attributed to its characteristic structure in which the double bond is protected by robust adamantyl frameworks to prevent normal 1,2-addition. Reactions with chlorine,[2] nitronium,[2b,3] nitrosonium,[2b,3] benzenesulfenyl chloride,[4] and benzeneselenenyl chloride[5] have been investigated, and the bridged species were considered as reaction intermediates. In addition, the central double bond of **1-H** is forced to twist by the introduction of substituents at adjacent positions. Lenoir et al. reported the synthesis of *trans*-dimethyl- and *trans*-diethyl-substituted 2,2′-biadamantylidenes (**1-Me** and **1-Et**, respectively) with twisted double bonds by the McMurry coupling.[6] They indicated that the double bond becomes more distorted with increasing bulkiness of the substituents and that **1-Et** has a twist angle of 12.3°, as determined by X-ray single-crystal analysis. Recently, bromination of **1-Me** was reported to give bromide **3** via a bridged bromonium ion **2-Me**, although this ion was not sufficiently stable to be isolated.[7]

SCHEME 1

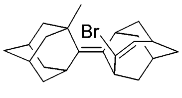




1-H (R = H)
1-Me (R = Me)
1-Et (R = Et)
1-Ph (R = Ph)



2-R



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Introduction of a substituent bulkier than an ethyl group to **1-H** is expected to twist the double bond further, which can lead to different reaction behavior. The free-energy difference between the equatorial and axial conformers of phenylcyclohexane is estimated to be about 1 kcal/mol larger than that for ethylcyclohexane (Scheme 1).[8] Therefore, the phenyl derivative, *trans*-2,2′-bi(1-phenyladamantylidene) (**1-Ph**), is expected to be more distorted at the double bond. We now report the synthesis and reaction behavior of **1-Ph**. The molecular structure, in particular the twist angles of double bonds, was determined by single-crystal X-ray analysis. Oxidation potentials of **1-Ph** were measured by cyclic voltammetry, and its electrophilic reaction with bromine was investi-

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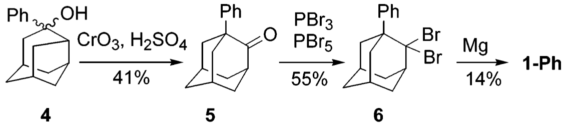
10.1021/jo020247+ CCC: $22.00

TABLE 1. Selected Bond Lengths, Bond Angles, and Torsion Angles for 1-Ph Determined by X-ray Crystallographic Analysis

bond length, Å		bond angle, deg		torsion angle, deg	
C(2)−C(2′)	1.351(4)	C(1)−C(2)−C(2′)	127.1(3)	C(1)−C(2)−C(2′)−C(1)	167.2(3)
C(1)−C(2)	1.548(3)	C(3)−C(2)−C(2′)	123.0(3)	C(1)−C(2)−C(2′)−C(3′)	−23.2(2)
C(2)−C(3)	1.538(3)	C(1)−C(2)−C(3)	109.2(2)	C(3)−C(2)−C(2′)−C(3′)	146.3(4)
C(1)−C(11)	1.529(3)	C(2)−C(1)−C(11)	116.0(2)	C(3)−C(2)−C(2′)−C(1′)	−23.2(2)
		C(8)−C(1)−C(11)	112.6(2)		
		C(9)−C(1)−C(11)	104.4(2)		

SCHEME 2



gated. The results are compared with those for the parent alkene and other substituted 2,2′-biadamantylidenes.

Results and Discussion

Synthesis. The synthetic method for *trans*-2,2′-bi(1-phenyladamantylidene) (**1-Ph**) is shown in Scheme 2. The Jones oxidation[9] of a mixture of *exo*- and *endo*-4-phenyl-4-protoadamantanols (**4**)[10−12] yielded 1-phenyl-2-adamantanone (**5**). Then, ketone **5** was converted to 2,2-dibromo-1-phenyladamantane (**6**) by treatment with a mixture of PBr_3 and PBr_5.[13,14] Subsequent reductive coupling of **6** with magnesium produced the desired olefin **1-Ph**, which contained a small amount of unknown hydrocarbons. Following preparative recycling GPC and repeated recrystallization, pure **1-Ph** was obtained as colorless crystals in 14% yield.

^{13}C NMR measurements showed six aliphatic and five aromatic and olefinic signals, and the quarternary C(2)/C(2′) resonance appeared at δ 152.8. The H(3) proton signal appeared at δ 2.17, the assignment of which is based on the HETCOR measurement. This proton is largely shielded compared to the corresponding proton in **1-H** (δ 2.90).

In preliminary studies, we attempted the modified McMurry coupling of **5**, which is generally useful for the preparation of a symmetric olefin from a ketone,[15,16] but the reduction of **5** using a low-valence titanium reagent ($TiCl_4$/Zn) resulted in quantitative formation of undesired 1-phenyl-2-adamantanol,[10,17] presumably due to difficulty of association due to steric hindrance.

Molecular Structure. The molecular structure of **1-Ph** obtained by X-ray crystallographic analysis is depicted in Figure 1. Selected bond distances, bond angles, and torsion angles are summarized in Table 1.

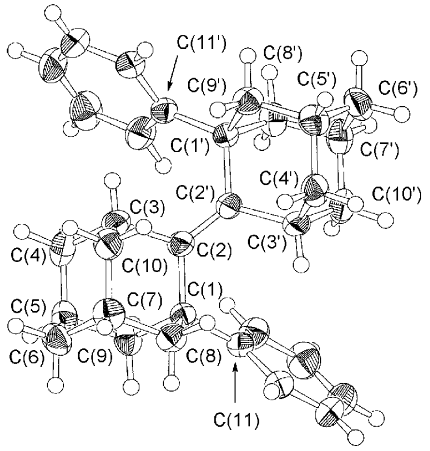
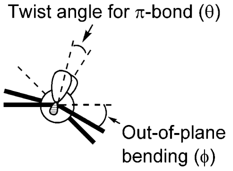


FIGURE 1. ORTEP drawing for the molecular structure of **1-Ph** determined by single-crystal X-ray diffraction analysis.

SCHEME 3



Twist angles, out-of-plane bendings,[24] and bond lengths of the double bonds shown in Scheme 3 are summarized in Table 2. The central π-bond has a twist angle (θ) of 23.2°, showing marked distortion due to the steric repulsion between a phenyl substituent and the adamantyl group on the opposite side. The twist angle is larger than that reported for **1-H** (0.0°) [18] and that for **1-Et** (12.3°).[6b] The central double bond (1.351 Å) is elongated in comparison with that of **1-H** (1.336 Å) and is as long as that for **1-Et** (1.358 Å). Other noticeable distortions can be seen at bending angles around C(1) and C(2) carbons. The bond angle of C(2)−C(1)−C(11) is larger than those of C(8)−C(1)−C(11) and C(9)−C(1)−C(11), and the angle of C(1)−C(2)−C(2′) is also larger than that of C(3)−C(2)−C(2′) by 4°. The olefinic C(2) carbon is considerably pyramidalized with an out-of-plane angle of 10.5°. Moreover, C(1)−C(9) and C(3)−C(10) (1.557, 1.554 Å) are slightly longer than C(1)−C(8) and C(3)−C(4) (1.547, 1.534 Å), respectively, which is also indicative of the distortion of the adamantyl framework. The torsion angles around the double bond indicate that the olefin has a twisted/syn-folded conformation.[19]

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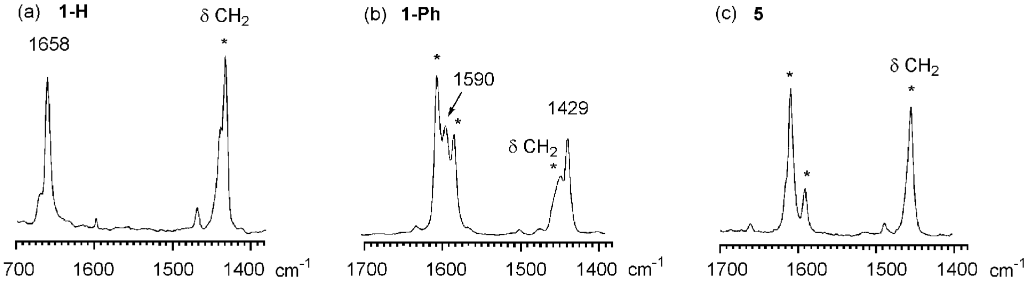

FIGURE 2. Raman spectra for **1-H** (a), **1-Ph** (b), and **5** (c). An asterisk (*) denotes observed signals by IR spectroscopy.

TABLE 2. Twist Angles (θ), Out-of-Plane Bendings (ϕ), and Bond Lengths of the C(2)=C(2′) π-Bond for 1-H, 1-Et, and 1-Ph Obtained by MM3, PM3, HF, and BLYP Calculations Including the Results of X-ray Diffraction Analysis

olefin	theory	twist angle for π-bond (θ), deg	out-of-plane bendings (ϕ), deg	C(2)=C(2′) bond length, Å
1-H	X-ray	0.0[a]	0.0[a]	1.336[a]
	MM3	0.0	0.0	1.356
	PM3	0.0	0.0	1.341
	RHF/6-31G(d)	0.0	0.0	1.332
	BLYP/6-31G(d)	0.0	0.0	1.361
1-Et	X-ray	12.3[b]	8.9[b]	1.358[b]
	MM3	38.7	15.4	1.362
	PM3	34.2	10.9	1.354
	RHF/6-31G(d)	11.8	5.4	1.348
	BLYP/6-31G(d)	25.0	6.3	1.377
1-Ph	X-ray	23.2	10.5	1.351
	MM3	24.1	14.5	1.364
	PM3	26.3	13.6	1.352
	RHF/6-31G(d)	21.7	6.4	1.343
	BLYP/6-31G(d)	21.4	7.3	1.372

[a] Ref 18. [b] Ref 6b.

TABLE 3. Stretching Frequency for Double Bond by Raman Spectroscopy and HF/6-31G(d) Calculations

olefin	raman, cm^{-1}	HF/6-31G(d), cm^{-1} [a]
1-H	1658[b]	1683
1-Me	1592[b]	1620
1-Et	1572[b]	1599
1-Ph	1590	1617

[a] Values after scale factor correction. [b] From ref 6.

The distance between H(3) and the ipso carbon of a benzene ring, C(11′), is measured to be only 2.37 Å, whereas the sum of the van der Waals radius of hydrogen (1.2 Å) and the thickness of the π-electron cloud (1.7 Å) of a phenyl substituent is 2.9 Å.[20] The close proximity accounts for the 0.73 ppm shielding for H(3) observed in the ^{1}H NMR spectrum (see above).[21]

The structures for **1-H**, **1-Et**, and **1-Ph** were computed with the MM3,[22] PM3,[23] HF, and DFT methods. Selected data are summarized in Table 2. All the optimized structures are symmetrical. MM3 and PM3 methods have a tendency to overestimate bending and twisting distortions. The twist angles and bond lengths calculated by HF/6-31G(d) are closer to those determined by X-ray analysis than those determined by BLYP/6-31G(d). Therefore, HF/6-31G(d) calculation data are used for the following discussion.

Raman Spectroscopy. Vibrations of the central double bonds are inactive in IR spectroscopy but active in Raman due to the symmetrical structural form of **1-Ph**. Observed Raman spectra are shown in Figure 2. The obtained spectrum for **1-H** is in agreement with the literature data reported by Lenoir.[6] The spectrum for **1-Ph** showed five peaks, among which two peaks, 1590 and 1429 cm^{-1}, were found to be IR inactive by IR spectroscopy. The other three signals, which can be attributed to phenyl ring stretchings and CH$_2$ scissoring vibrations, have frequencies similar to those for **5**. HF/6-31G(d)//HF/6-31G(d) frequency calculations indicate that the C=C stretching has a frequency of 1617 cm^{-1} with Raman activity and small IR activity and that the signal 1429 cm^{-1} should be CH$_2$ scissoring vibration. Therefore, the IR inactive 1590 cm^{-1} signal is assigned to the C=C stretching vibration. This stretching frequency is 68 cm^{-1} smaller than that of **1-H**, 1658 cm^{-1}, and similar to that of **1-Et**, 1572 cm^{-1} (Table 3). This observation suggests that the bond strength in **1-Ph** is not weakened significantly compared with that of **1-Et**, though **1-Ph** is more twisted than **1-Et**.

Cyclic Voltammetry. The redox behavior of **1-Ph** was examined by cyclic voltammetry in acetonitrile (Figure 3). A reversible oxidation wave was observed at 0.87 V vs Fc/Fc$^+$ ($E_{1/2}$), which is lower by 0.19 V than the $E_{1/2}$ of **1-H** (1.06 V vs Fc/Fc$^+$).[25] Differential pulse voltammetric measurements (DPV) also gave essentially the same oxidation potentials. The decrease in the oxidation potential suggests an increase in the HOMO energy level due to a loss of the overlap of p-orbitals by twisting, which is corroborated by theoretical calculations. HF/6-31G(d) calculations show a rise in the HOMO energy level from −8.41 eV for **1-H** to −8.11 eV for **1-Ph**.

Reactions with Bromine and Trifluoroacetic Acid. Dropwise addition of 0.9 equiv of bromine to **1-Ph** in dichloromethane at room temperature led to clean forma-

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(25) (a) The observed $E_{1/2}$ of **1-H** (1.06 V vs Fc/Fc$^+$ = 1.43 V vs SCE) is close to reported values of 1.43 V in 7:3 acetonitrile−dichloromethane and 1.45 V vs SCE in acetonitrile (refs 25b and 26, respectively). The $E_{1/2}$ vs SCE was calculated by an equation of $E_{1/2}$ (vs Fc/Fc$^+$) + 0.374 V vs SCE taken from ref 25b. (b) Komatsu, K.; Kamo, H.; Tsuji, R.; Takeuchi, K. *J. Org. Chem.* **1993**, *58*, 3219.

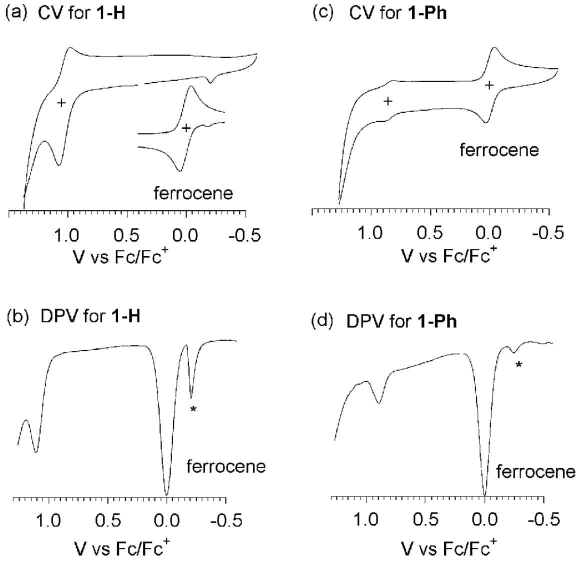
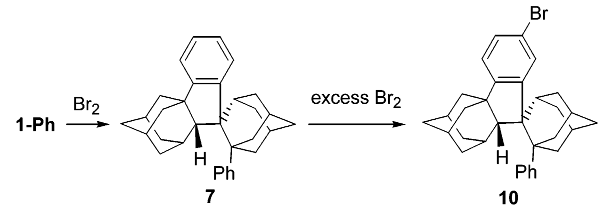


FIGURE 3. Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) for **1-H** (a and b) and **1-Ph** (c and d) in acetonitrile containing 0.1 M *n*-Bu_4NClO_4. An asterisk (*) denotes peaks for impurities.

SCHEME 4



tion of hydrocarbon **7** (Scheme 4). On addition of the initial portions of bromine, the color immediately disappeared, but it persisted thereafter. The mass spectrum (FAB+, NPOE) of **7** shows *m*/*e* 421 (M^+ + H) and 420 (M^+) signals as a hydrocarbon $C_{32}H_{36}$ and that there are no isotope peaks due to the presence of bromine. A single crystal was analyzed by the X-ray diffraction method, which revealed the structure of **7** as shown in Figure 4. NMR and elemental analytical data are in agreement with the above structure. A doublet peak that was assigned to *m*-CH (Figure 4) was observed at a lower field, δ 8.19, than other aromatic signals. The exceptionally large deshielding is attributed to the influence of the ring current of the adjacent phenyl substituent.[21]

A possible mechanism for the formation of **7** is shown in Scheme 5. Initially, bromine attacks the central double bond to produce a bridged bromonium ion or the corresponding open cation. Then the formation of a C−C bond and subsequent loss of a proton gives bromide **8**. Once a small amount of proton is formed, acid-catalyzed intramolecular Friedel−Crafts alkylation converts the rest of **1-Ph** to **7**.[27] This mechanism is supported by the fact that treatment of **1-Ph** with trifluoroacetic acid in chloroform yielded the same product **7** quantitatively.

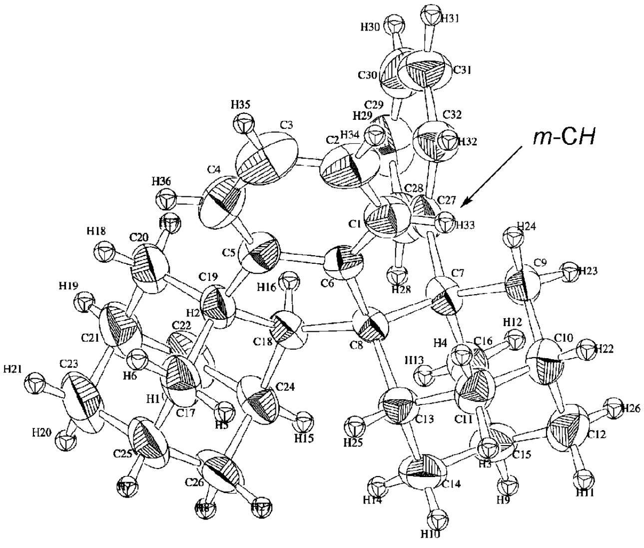
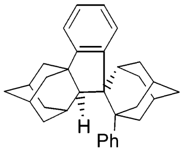


FIGURE 4. ORTEP drawing for the structure of **7** determined by single-crystal X-ray diffraction analysis (proton labeled as *m*-C*H* is exceptionally deshielded in NMR).

Direct observation of the reaction solution by ^1H NMR analysis showed the clean formation of **7** in 5 min at room temperature. Similar acid-catalyzed Friedel−Crafts reaction was reported by Mitchell and Zhang[28] for dehydropyrene derivatives. The NMR spectra showed no indication of the formation of diastereomer **9**. PM3 calculations indicated that compound **7** is more stable than isomer **9** by 6 kcal/mol.



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When bromination was carried out using excess bromine under similar conditions, a brominated compound **10** was obtained (Scheme 4). The NMR spectra of **10** are very similar to **7** except for signals in the aromatic region. One aromatic CH carbon disappeared, and a remarkably shielded aromatic quarternary carbon (at δ 118.5) was observed instead. The multiplicity of the most deshielded (δ 8.19) aromatic proton signal in **7**, which was assigned to *m*-C*H* (Figure 4), was changed to a singlet (δ 8.31). These findings suggest that bromination occurred at the carbon next to *m*-CH.

The reaction with a stronger acid, CF_3SO_3H, gave a mixture of products with no clearly distinguishable NMR signals.

Conclusions

A highly congested olefin, **1-Ph**, was synthesized by Grignard coupling of a geminal dibromide. This method is supposed to be effective for the synthesis of highly congested olefins that are difficult to synthesize by McMurry coupling. X-ray single-crystal analysis indicated that the double bond is twisted by 23.2°, which is

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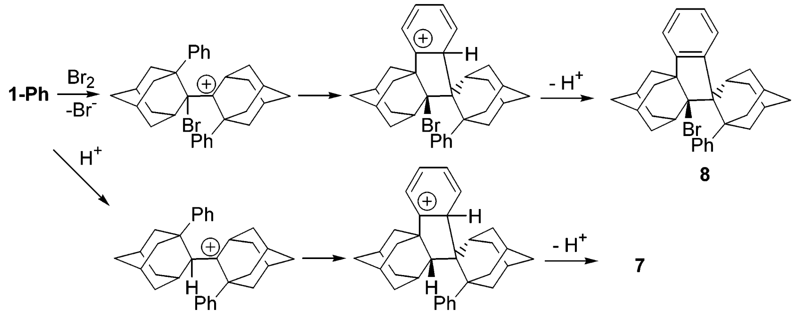
SCHEME 5



the most twisted double bond among those of known 2,2′-biadamantylidenes. **1-Ph** underwent anodic oxidation to give a radical cation more easily than **1-H** with a normal planar double bond. The radical cation is sufficiently stable to show a reversible oxidation wave, but the cationic intermediate in the electrophilic reaction with bromine and trifluoroacetic acid is unstable, giving **7** at room temperature. The enhanced reactivity is consistent with the observation by Chiappe et al.[7] that the bridged bromonium ion from **1-Me** with a twisted double bond is more reactive than that from **1-H**.

Experimental Section

Melting points are uncorrected. NMR spectra were recorded on 400 and 270 MHz instruments. IR was obtained by using FT-IR spectrophotometer. Raman experiments were performed on powdered samples. FAB mass spectra were obtained using *o*-nitrophenyl octyl ether as a matrix in the positive mode. Elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto. 2,2′-Biadamantylidene (**1-H**)[15] and *exo*- and *endo*-4-phenyl-4-protoadamantanol (**4**)[10−12] were prepared by literature procedures. Tetra-*n*-butylammonium perchlorate was recrystallized from 5:1 AcOEt−hexane. Anhydrous solvents for syntheses were purified by standard procedures. Other commercially available reagents were of reagent-grade quality and used as received. Medium-pressure liquid chromatography (MPLC) was conducted on silica gel (45−75 μm). Recycle preparative HPLC was performed with GPC columns (ϕ 20 mm × 600 mm) using $CHCl_3$ as an eluent.

1-Phenyl-2-adamantanone (5). To a solution of *exo*- and *endo*-4-phenyl-4-protoadamantanol (**4**, 8.5 g, 37 mmol) in acetone (1.0 L) was added dropwise a solution of CrO_3 (15 g, 150 mmol) in H_2SO_4 (12.4 mL). After being stirred for 24 h, the mixture was filtered, and most of the solvent was evaporated. The resulting mixture was diluted with water and extracted by ether, and the ether solution was dried ($MgSO_4$). Removal of the solvent afforded brown crystals, recrystallization of which from hexane gave 1-phenyl-2-adamantanone (**5**) as colorless crystals (3.4 g) in 41% yield: mp 140.0−140.5 °C; IR (KBr, cm^{-1}) 2900, 1712, 1444, 1064, 742, and 695; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.91 (m, 1H), 2.00 (m, 1H), 2.11−2.30 (m, 8H), 2.44 (m, 2H), 2.73 (brs, 1H), 7.22−7.29 (m, 3H), 7.36 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 28.3 (2CH), 35.6 (CH_2), 39.2 ($2CH_2$), 45.0 ($2CH_2$), 47.4 (CH), 53.9 (C), 126.6 (CH), 126.9 (2CH), 127.9 (2CH), 142.4 (C), 215.2 (C). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.77; H, 8.05.

2,2-Dibromo-1-phenyladamantane (6). To a solution of **5** (1.50 g, 6.6 mmol) in PBr_3 (23 mL) was added PBr_5 (4.9 g, 11 mmol) in small portions over a period of 1.5 h. After being stirred for 24 h, the reaction mixture was diluted with ice−water and extracted with ether. The extract was washed with saturated $NaHCO_3$ and water and dried ($MgSO_4$). Evaporation of the solvent afforded a pale yellow oil, recrystallization of which from hexane gave 2,2-dibromo-1-phenyladamantane (**6**) (1.4 g) as colorless crystals in 55% yield: mp 172.5−173.5 °C; IR (KBr, cm^{-1}) 2904, 1494, 1442, 753, and 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69−1.88 (m, 6H), 2.16 (brs, 2H), 2.71−2.81 (m, 3H), 3.10 (d, J = 11.7 Hz, 2H), 7.27−7.38 (m, 3H), 7.63 (dd, J = 8.3, 1.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0 (2CH), 35.3 ($2CH_2$), 37.8 (CH_2), 39.3 ($2CH_2$), 48.4 (C), 49.5 (CH), 91.7 (C), 126.8 (2CH), 127.1 (CH), 128.4 (2CH), 143.8 (C). Anal. Calcd for $C_{16}H_{18}Br_2$: C, 51.92; H, 4.90. Found: C, 51.77; H, 4.85.

***trans*-2,2′-Bi(1-phenyladamantylidene) (1-Ph).** A solution of **6** (500 mg, 1.4 mmol) in dry ether (42 mL) with magnesium (0.7 g, 29 mmol) was heated to reflux under N_2. Then, 1,2-dibromoethane (2.5 mL, 29 mmol) was added dropwise over a period of 2 h. After the solution had been refluxed with stirring for an additional 15 h, water was carefully added. The resulting mixture was extracted with ether and $CHCl_3$. The combined organic layers were washed with saturated NaCl and dried ($MgSO_4$). Removal of the solvent afforded a pale yellow oil, which upon recycle HPLC and recrystallization three times from hexane and once from $CHCl_3$ gave pure *trans*-2,2′-bi(1-phenyladamantylidene) (**1-Ph**) as colorless crystals (41 mg, 14%): mp 278.5−280.0 °C; IR (KBr, cm^{-1}) 2912, 1599, 1492, 1442, 752, and 698; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.31 (dd, J = 12.0, 2.7 Hz, 4H), 1.45 (d, J = 12.2 Hz, 4H), 1.60 (s, 4H), 1.85 (d, J = 11.7 Hz, 4H), 1.94 (brs, 4H), 2.08 (d, J = 2.7 Hz, 4H), 2.17 (t, J = 2.4 Hz, 2H), 7.14 (dd, J = 7.3, 7.3 Hz, 2H), 7.33 (dd, J = 7.6, 7.6 Hz, 4H), 7.44 (dd, J = 7.3, 7.3 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 28.6 (4CH), 36.3 ($2CH_2$), 36.7 (2CH), 38.2 ($4CH_2$), 44.9 (2C), 46.0 ($4CH_2$), 124.7 (2C), 125.1 (4CH), 128.1 (4CH), 140.0 (2C), 152.8 (2C). Anal. Calcd for $C_{32}H_{36}$: C, 91.37; H, 8.63. Found: C, 90.77; H, 8.82.

Reaction of *trans*-2,2′-Bi(1-phenyladamantylidene) (1-Ph) with Bromine. To a solution of **1-Ph** (120 mg, 0.30 mmol) in CH_2Cl_2 (9.5 mL) was added dropwise 3.2×10^{-2} M bromine in CH_2Cl_2 (0.8 mL) in the dark. After the solution had been stirred overnight, the solvent was evaporated to give a pale yellow oil, which was analyzed by NMR to show almost quantitative formation of **7**. HPLC with GPC columns and recrystallization from hexane gave pure **7** (51 mg, 41%) as colorless prisms, which were used for X-ray crystallographic analysis: mp 206.5−207.0 °C (from hexane); IR (KBr, cm^{-1}) 2898, 2848, 1596, 1496, 1468, 1447, 750, and 697; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.99 (d, J = 11.2 Hz, 1H), 1.47 (d, J = 7.9 Hz, 2H), 1.58 (brs, 1H), 1.80 (m, 14H), 2.14 (s, 1H), 2.30 (d, J = 12.5 Hz, 3H), 2.53 (d, J = 13.2 Hz, 1H), 2.89 (brs + d, J = 15.5 Hz, 2H), 3.00 (d, J = 12.5 Hz, 1 H), 3.51 (d, J = 13.5 Hz, 1H), 6.89 (dd, J = 7.3, 1.3 Hz, 2H), 6.96 (brs, 2H), 7.14 (d, J = 7.3 Hz, 2H), 7.20 (m, 2H), 8.19 (d, J = 7.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 28.2 (CH), 28.4 (CH), 29.0 (CH), 29.1 (CH), 33.3 (CH_2), 33.7 (CH_2), 34.2 (CH_2), 34.4 (CH), 35.9 (CH), 36.9 (CH_2), 39.6 (CH_2), 39.9 (CH_2), 40.4 (CH_2), 41.4 (CH_2), 43.5 (CH_2), 43.7 (C), 44.4 (CH_2), 45.7 (C), 54.1 (CH), 60.6 (C), 121.2 (CH), 124.9 (CH), 125.3 (CH), 126.4 (CH), 126.9 (2CH), 127.6 (2CH), 130.5 (CH), 146.8 (C), 147.8 (C), 153.4 (C). Anal. Calcd for $C_{32}H_{36}$: C, 91.37; H, 8.63. Found: C, 91.21; H, 8.65.

Reaction of **1-Ph** (5.0 mg, 0.012 mmol) in CH_2Cl_2 (2.0 mL) with 0.65 M bromine in CH_2Cl_2 (0.17 mL) gave a mixture of **10** and several unknown compounds as a pale yellow oil. HPLC purification gave **10** as a major component (16% yield): pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.96 (d, J = 11.2 Hz, 1H), 1.44 (d, J = 7.9 Hz, 2H), 1.50−1.95 (m, 14H), 2.17 (s, 1H), 2.30 (m, 3H), 2.51 (d, J = 13.2 Hz, 1H), 2.80 (d, J = 15.5 Hz, 1H), 2.85 (brs, 1H), 2.98 (d, J = 12.5 Hz, 1 H), 3.41 (d, J = 13.5 Hz, 1H), 6.86 (d, J = 7.3 Hz, 1H), 7.00 (brs, 2H), 7.20−7.40 (m, 4H), 8.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0 (CH), 28.2 (CH), 28.8 (CH), 28.9 (CH), 33.1 (CH_2), 33.5 (CH_2), 34.0 (CH_2), 34.3 (CH), 35.8 (CH), 36.8 (CH_2), 39.5 (CH_2), 39.7 (CH_2), 40.1 (CH_2), 41.2 (CH_2), 43.2 (CH_2), 43.5 (C), 44.3 (CH_2), 45.6 (C), 54.1 (CH), 60.9 (C), 118.5 (C), 122.6 (CH), 125.5 (CH), 126.9 (2CH), 127.5 (2CH), 129.4 (CH), 133.2 (CH), 147.3 (C), 149.3 (C), 152.3 (C).

Reaction of 1-Ph with Trifluoroacetic Acid. A solution of **1-Ph** (1.7 mg, 4.0×10^{-3} mmol) in $CDCl_3$ (0.45 mL) containing CF_3COOH (0.03 mL) was allowed to react at room temperature overnight. The resulting mixture was analyzed by NMR measurements, which indicated that only **7** had been formed.

Calculations. Semiempirical PM3 results were obtained with the MOPAC package.[23] Empirical molecular mechanics calculations were performed through the MM3(92)[22] program. HF and DFT calculations were performed using Gaussian 98 software.[29] Geometry optimizations were verified by frequency calculations (Tables of Cartesian coordinates, energies, and number of imaginary frequencies are provided as Supporting Information).

Single-Crystal X-ray Crystallographic Analysis of 1-Ph and 7. Data were collected at room temperature. The structure was solved by direct methods using SIR92 for **1-Ph** and SHELXS-97[30] for **7**.

1-Ph: $C_{32}H_{36}$, MW = 420.64. Crystal data: 0.20 × 0.20 × 0.20 mm, monoclinic, space group $C2/c$, a = 19.768(4) Å, b = 6.721(8) Å, c = 18.437(5) Å, β = 110.60(2)°, V = 2292(2) Å^3, Z = 4, d_{calcd} = 1.218 g/cm^3, λ (Mo Kα) = 0.71069 Å, μ = 0.68 cm^{-1}, R = 0.048, R_w = 0.043.

7: $C_{32}H_{36}$, MW = 420.64. Crystal data; 0.40 × 0.30 × 0.30 mm, monoclinic, space group $P2_1/n$, a = 10.270(7) Å, b = 22.193(7) Å, c = 10.763(8) Å, β = 112.01(5)°, V = 2274(2) Å^3, Z = 4, d_{calcd} = 1.228 g/cm^3, λ (Mo Kα) = 0.71069 Å, μ = 0.69 cm^{-1}, R = 0.049, R_w = 0.049.

Cyclic Voltammetry. Cyclic voltammograms were obtained with a system with a three-electrode cell composed of a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/$AgNO_3$ (0.01 M in CH_3CN) reference electrode. The observed potentials were corrected with reference to ferrocene added as an internal standard.

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Supporting Information Available: Selected NMR spectra for **1-Ph**, **7**, and **10**, calculated energies and Cartesian coordinates for **1-H**, **1-Et**, and **1-Ph** optimized by HF and DFT calculations, and results of X-ray analysis for **1-Ph** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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